UNIVERSITI PUTRA MALAYSIA

GRAFT COPOLYMERISATION OF 2-HYDROXYETHYL METHACRYLATE ONTO SAGO STARCH

RAFEADAH RUSLI

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By

RAFEADAH RUSLI

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UPM

Abstract of thesis submitted to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

GRAFT COPOLYMERISATION OF 2-HYDROXYETHYL METHACRYLATE ONTO SAGO STARCH

By

RAFEADAH BINTI RUSLI

February 2001

Chairman: Professor Wan Md. Zin Wan Yunus, Ph.D.

Faculty : Science and Environmental Studies

Studies on the preparation of 2-hydroxyethyl methacrylate (HEMA) grafted sago starch were conducted using ceric ammonium nitrate (CAN) and potassium persulphate (PPS) as the free radical initiators under a nitrogen atmosphere. The effect of various parameters on the grafting process was determined. The optimum conditions obtained for the grafting of HEMA onto sago starch using CAN as the initiator were as follows: reaction period, 3 h; reaction temperature, 40 °C; HEMA amount, 0.17 mol and CAN amount, 1.0 x 10^{-3} mol. Meanwhile the optimum conditions for the copolymer preparation using PPS as the initiator were as follows; reaction period, 2 h; temperature, 40 °C; amount of PPS, 5.0 x 10^{-3} mol and amount of HEMA, 0.05 mol. The percentage of grafting and grafting efficiency under optimum conditions for CAN initiation were 200% and 46%, respectively whereas for PPS initiation were 406% and 63%, respectively.

Fourier transform infrared (FTIR) spectroscopy, thermogravimetric analysis (TGA) and scanning electron microscopy (SEM) were used to characterise the graft copolymer. The infrared spectra of grafted copolymer in contrast to starch showed an additional peak at 1726 cm^{-1}, indicating the presence of ester carbonyl of the monomer. TGA studies revealed that the decomposition temperatures of starch were different from poly(HEMA) grafted sago starch. SEM studies indicated that HEMA was homogeneously grafted onto starch. The biodegradability study by using α-amylase revealed that the hydrolysis rate of the polysaccharide chains by α-amylase was strongly dependent on the percentage of grafting where the hydrolysis rate increased with the decrease in percentage of grafting. The highest hydrolysis rate was obtained by using 50 ppm of α-amylase concentration. The swelling behaviour of poly(HEMA) grafted sago starch in water and salt ions showed that the percentage of swelling at equilibrium increased as the percentage of grafting increased. The percentage of swelling at equilibrium and the swelling rate coefficient decreased in the order of water > NaCl > KCl > $MgCl_2$ > $CaCl_2$. The water diffusion of the grafted polymer in water and cationic salt solutions was a Fickian character. The study of metal chelating properties indicated that Cibacron Blue-attached grafted polymer particles have higher affinity towards Cd(II) and Pb(II) as compared to Fe(III) and Cu(II). The dye-attached grafted polymer also showed high affinity for these metal ions between pH 4 and 7.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

PENGKOPOLIMERAN CANGKUK 2-HIDROKSIETIL METAKRILAT KE ATAS KANJI SAGU

Oleh

RAFEADAH RUSLI

Februari 2001

Pengerusi : Profesor Wan Md. Zin Wan Yunus, Ph.D.

Fakulti : Sains dan Pengajian Alam Sekitar

Kajian mengenai penyediaan dan pencirian kopolimer kanji sagu-2-hidroksietil metakrilat (HEMA) dilakukan dengan menggunakan serium ammonium nitrat (SAN) dan kalium persulfat (KPS) sebagai pemula radikal bebas di bawah atmosfera nitrogen. Parameter-parameter yang mempengaruhi tindak balas pengkopolimeran turut dikenalpasti. Keadaan optimum yang diperolehi bagi proses pengcangkukkan HEMA ke atas kanji sagu menggunakan SAN sebagai pemula adalah seperti berikut: masa tindak balas, 3 jam; suhu tindak balas, 40 °C; amaun HEMA, 0.17 mol dan amaun SAN, 1.0×10^{-3} mol. Manakala keadaan optimum untuk penyediaan kopolimer menggunakan KPS sebagai pemula adalah seperti berikut: masa tindak balas, 2 jam; suhu tindak balas, 40 ^{o}C; amaun kalium persulfat, 5×10^{-3} mol dan amaun HEMA, 0.05 mol. Peratus-peratus pengcangkukkan dan kecekapan pengcangkukkan di bawah keadaan optimum bagi pemula SAN adalah masing-masing 200% dan 46% manakala untuk pemula KPS masing-masing adalah 406% dan 63%.

Analisis–analisis spektroskopi inframerah transformasi fourier , termogravimetri dan mikroskop pengimbasan elektron digunakan untuk mencirikan pembentukan kopolimer cangkuk. Spektra inframerah kopolimer tercangkuk berbanding dengan kanji menunjukkan terdapatnya puncak tambahan pada 1726 cm^{-1} yang mengesahkan kehadiran karbonil ester monomer. Analisis termogravimetri pula menunjukkan bahawa suhu-suhu penguraian kanji adalah berbeza daripada kopolimer kanji sagu-HEMA. Kajian mikroskop pengimbasan elekron pula mendapati bahawa HEMA telah dicangkukkan ke atas kanji sagu secara homogenus. Kajian mengenai penguraian secara biologi dengan menggunakan ∝-amilase menunjukkan bahawa kadar hidrolisis rantai polisakarida bergantung kepada peratus pengcangkukkan di mana kadar hidrolisis bertambah dengan berkurangnya peratus pengcangkukkan. Kadar hidrolisis yang paling tinggi yang diperolehi adalah dengan menggunakan kepekatan ∝-amilase sebanyak 50.00 ppm.

Ciri pengembungan kopolimer kanji sagu-poli(HEMA) di dalam air dan larutan-larutan garam memperlihatkan peratus pengembungan pada keseimbangan meningkat apabila peratus pengcangkukkan meningkat. Peratus pengembungan pada keseimbangan dan pemalar kadar pengembungan menurun dalam turutan air > NaCl > KCl > $MgCl_2$ > $CaCl_2$. Pembauran di dalam air dan larutan-larutan garam kation ke dalam polimer tercangkuk bercirikan Fickian. Kajian mengenai ciri-ciri pengkelat logam menunjukkan molekul Sibakron Biru yang terikat pada polimer tercangkuk ini mempunyai affiniti yang tinggi terhadap Cd(II) dan Pb(II) berbanding dengan Fe(III)

dan Cu(II). Kopolimer tercangkuk yang telah ditambahkan pewarna juga mempunyai affiniti yang tinggi terhadap ion-ion logam ini di antara pH 4 and 7.

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I certify that an Examination Committee met on 28th February 2001 to conduct the final examination of Rafeadah Rusli on her Master of Science thesis entitled " Graft Copolymerisation of 2-Hydroxyethyl Methacrylate onto Sago Starch" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidate be awarded the revelant degree. Members of the Examination Committee are as follows:

Mahiran Basri, Ph.D.,
Associate Professor,
Faculty of Science and Environmental Studies
Universiti Putra Malaysia
(Chairman)

Wan Md. Zin Wan Yunus, Ph.D.,
Professor
Faculty of Science and Environmental Studies
Universiti Putra Malaysia
(Member)

Mansor Ahmad, Ph.D.,
Faculty of Science and Environmental Studies
Universiti Putra Malaysia
(Member)

Mohamad Zaki Abd. Rahman
Faculty of Science and Environmental Studies
Universiti Putra Malaysia
(Member)

MOHD GHAZALI MOHAYIDIN, Ph.D.,
Professor/Deputy Dean of Graduate School,
Universiti Putra Malaysia

Date: 14 MAY 2001

This thesis submitted to the Senate of Universiti Putra Malaysia has been accepted as fulfilment of the requirement for the degree of Master of Science.

AINI IDERIS, Ph.D,
Professor,
Dean of Graduate School,
Universiti Putra Malaysia.

Date: 14 JUN 2001

DECLARATION

I hereby declare that the thesis is based on my original work except for the quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.

Candidate:
RAFEADAH RUSLI

Date : 12/5/2001

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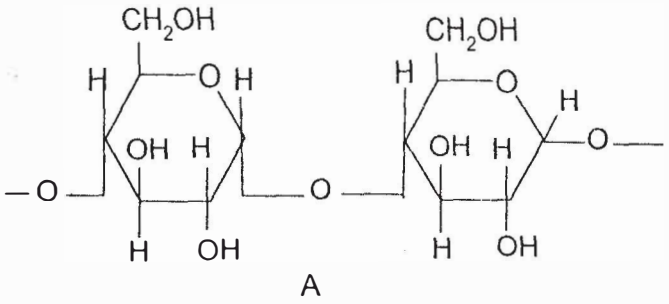
CHAPTER I

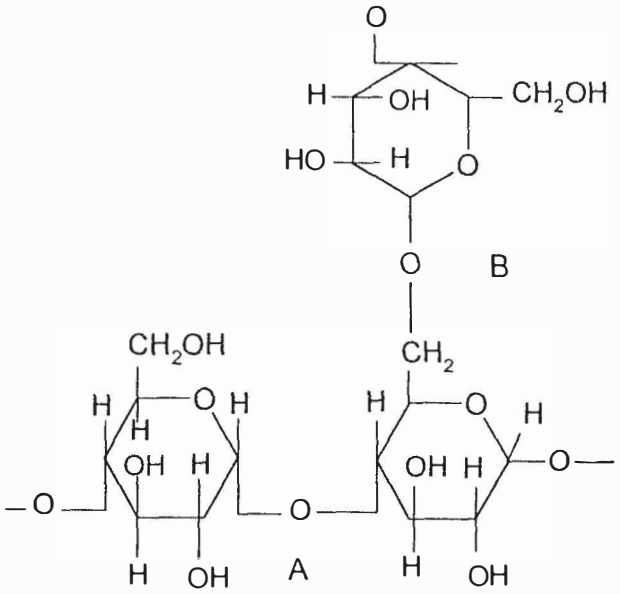
INTRODUCTION

Polysaccharides are carbohydrates consist of hundreds or even thousands of monosaccharide units per molecule where they are linked by glycoside linkages and can be broken by hydrolysis. Starch is one of the polysaccharides in nature and made up of the elements, carbon, hydrogen and oxygen. It is the predominant carbohydrate in all the major foods used by man such as potatoes, rice, maize and beans. Starch, which occurs abundantly in grains, tubers and fruits, is the major carbohydrate food for many species of animals and bacteria, therefore, is a link for these organisms to the energy of the sun. Starch occurs in living plants in the form of discrete granules ranging from about 5-40 μ in diameter, depending on the plant source. The starch granule is a natural way to store energy in green plants over long times. The granule is well suited to this role, being insoluble in water and densely packed, but still accessible to the plant's metabolic system. Native granules have crystallinity between 15 and 45% and can yield X-ray diffraction patterns, generally of low quality (Imberty et al., 1991).

Starch owes much of its functionality to two major high-molecular-weight carbohydrate components, amylose and amylopectin, as shown in Scheme 1. Amylose is a linear polymer of molecular weight between one thousand and one million, made up of several hundred glucose units linked by α 1-4 glycosidic linkages. Amylose tends to form hydrogen bonds intramolecularly as a loose helix due to its different steric arrangement. Together with amylopectin, amylose exists in



Amylose



Amylopectin

A = 1,4' ∝-glucosidic bond

B = 1,6' ∝-glucosidic bond

Scheme 1: Component Structure of Starch

plants as starch a material that plants use for storing energy and glucose units. Amylopectin is one of the biggest molecules in nature; it is a branched polymer of glucoses units with α 1-6 glycosidic linkages at the branching points and α 1-4 glycosidic linkages at the linear region. The molecular weight of amylopectin can run into several millions (Vaidya and Bhattacharya, 1994). The ratio of amylose to amylopectin is a characteristic of the starch source. Typical amylose contents are 20% for potato, 16.7% for tapioca, and 26% for wheat. Common varieties of rice and corn contain 18.5% and 28% amylose, respectively and waxy varieties contain 0%. Newer hybrids, such as the amylomaize hybrids of corn can contain 50-90% amylose (Jane et al., 1994). Variations in the branching pattern of amylopectin give starches with a wide variety of functional properties. Functional groups can be introduced into starches by a number of chemical modification techniques in order to provide starches with improved or specific properties to extend their usefulness in industrial application. Chemically modified starches generally have markedly altered physicochemical properties, compared to their parent starches, primarily depending on the molar substitution or the degree of substitution (DS) and the type of functional groups employed (Rutenberg and Solarek, 1984).

Sago Starch

The sago palm has a number of uses to suit the needs of changing times. In the past, the starch extracted from the sago palm (*Metroxylon spp.*) once formed an important source of food for the indigenous people. Today the main uses of sago starch are in the form of sweeteners, thickeners, confectioneries in food manufacturing, textile finishes, gelling agents and as animal food component.

Among the important species for sago starch production are *M. longispinum*, *M. sylvestre*, *M. microcanthum*, *M. sagu* and *M. rumphii*. Sago starch is produced on a semi-industrial scale in Malaysia and mainly extracted from the pith of the trunk after the palm reaches maturity. A mature palm can produce about 100-550 kg of sago starch (Ahmad et al., 1999). Sago starches are produced about 60 million tones annually in South East Asia (Wang et al., 1996).

The granules of sago starch are oval or egg-shaped, and some are of truncated oval form. The size is in the range 15 μm to 65 μm and the average particle size is around 30 μm. Sago starch possesses a C-type X-ray diffraction pattern which, consist of about 65% A-type and 35% B-type crystalline forms (Ahmad and Williams, 1998). When gelatinisation occurs, the swollen granules appear as smooth bag-shaped forms that are not destroyed by boiling. Sago starch has a gelatinisation temperature of 70 °C, which is quite high compared to other starches such as tapioca (66 °C), potato (63 °C) and maize starch (68 °C). Sago starch consists of 27% amylose and 73% amylopectin and its quality depend on interrelated factors such as supply and quality of water, mode of transport and method of extraction and purification processes (Wurzburg, 1989). Due to the larger size of the starch granules and higher amylose content, sago starch has higher peak viscosity compared to other starches (Radley, 1976; Ruziah, 1996).

2-Hydroxyethyl Methacrylate (HEMA)

HEMA is a methacrylic ester, which has been substituted with a hydroxyl group. HEMA is polar due to its ester function, and the polarity is larger than that only with ester groups as an alcohol group bound to a flexible segment $-CH_2-CH_2-$. Poly(HEMA) is among the major synthetic polymers approved by federal agencies such as the Food and Drug Administration in the United States for industrial, pharmaceutical and biomedical applications. It is one of the most widely used hydrophilic polymers in medicine, and has found a wide variety of biomedical applications due to its high biocompatibility. In different forms, poly (HEMA) has also been used for enzyme immobilization, for controlled release of drugs, immobilization of cells, in immunochemical studies and as sorbents in chromatography (Denizli and Piskin, 1995).

Enzymatic Degradation of Starch

The starch is biodegradable where in a period of time, the starch looses its integrity and gets reduced to particles small enough to give minimal damage to the environment. Starch hydrolyzates are formed as a result of hydrolysis of starch into low-molecule carbohydrates, taking place under the action of either acids or enzymes. The production of starch hydrolyzates is influenced by the genesis of starch, which is associated with the shape and size of starch grains, as well as with the proportion by quantity of amylose to amylopectin, the content of fat, proteins and non-starch polysaccharides in the raw product (Nebesny et al., 1998). α-Amylase, a group of enzymes occurring in a wide variety of organisms catalyse the

hydrolysis of the α-1,4-glycosidic bonds in amylose, amylopectin and related oligosaccharides. It acts randomly with an endo-mechanism so that all the 1→4 links are completely hydrolysed, producing a mixture of D-glucose, maltose and low molecular weight α-limit-dextrin (1→6 branch points left intact) (Rath and Singh, 1998). In general, the enzyme either erode the entire /sections of the granular surface or digests channels from selected points on the surface toward the centre of the granule. On reaching the centre, enzyme attack proceeds outward over a broader front (Wang et al., 1995). Five general patterns of the attack mode of amylases on starch granules have been identified as pin-holes/pepper-potting; sponge-like erosion; many medium sized holes; distinct loci leading to single holes in individual granules and surface erosion (Evers, 1979).

Swelling

Interest in swellable polymeric systems has increased considerably due to their versatile applications in biomedicine, biotechnology and in a vast field where controlled release of chemicals is required. The swelling equilibrium of networks, according to the basic Flory-Rehner idea, results from a balance between the osmotic pressure acting to swell the network and the elastic pressure due to the stretching of the chains. The rubber elasticity theory assumes that the latter is the simple sum of contributions from changes in the distribution of configurations of individual strands (Skouri et al., 1995). The force of friction has to be taken into account during the process of swelling. The beginning of swelling consists of several processes coupled together: interaction with the solvent, time-dependent

solvent penetration inside the network, which induces a polymer density gradient and leads to the appearance of stress (Budtova and Sulaimenov, 1997).

The diffusion phenomena in systems of polymers and solvents were studied to clarify the polymer behaviour. The characteristic time of swelling is proportional to the square of a linear dimension and the diffusion coefficient of the polymer network. The diffusion of solvents in polymers depends strongly on concentration. Diffusion may be considered constant only at penetrant concentrations of a few hundredths of a percent. Most polymers swelling experiments will entail solvent-polymer volume ratios of the order of 2:1 up to as high as 6:1 (Buckley and Berger, 1962).

Chelating Polymer

Heavy metals are among the most important contaminants in water sources and have become a major concern due to their toxicity to many life forms. Among the traditional techniques for removal of heavy metals are chemical precipitation, solvent extraction, ion exchange and membrane processes. The use of specific sorbent has recently been considered as one of the promising techniques. Specific sorbents consist of a ligand (ion-exchange material or chelating agents) that interacts with the metal ions, and a carrier matrix that may be an inorganic material or polymer microbeads. As carrier matrices, polymers can easily be produced with a wide variety of compositions, and modified into specific sorbents, by introducing a variety of ligands.